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(54) Title: PROCESS FOR MANUFACTURING GLYCIDOL

(57) Abstract: Process for manufacturing glycidol comprising at least the following steps: a) glycerol and a chlorinating agent are reacted to form monochloropropanediol in a first reaction medium; and b) at least one part of the reaction medium from step a) is reacted with at least one basic compound to form glycidol and a salt in a second reaction medium, the organic component of which has a monochloropropanediol content before reaction with the basic compound greater than 100 g/kg of organic component.

Process for manufacturing glycidol

The present patent application claims the benefit of the French Patent application FR 07/56790 filed on 30 July 2007 and of the United States Provisional Patent Application USP 61/013713 filed on 14 December 2007, the content of both of which is incorporated herein by reference.

5 The present invention relates to a process for manufacturing glycidol.

Glycidol may be obtained by epoxidation of allyl alcohol using hydrogen peroxide or peracetic acid (K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, Third, Completely Revised Edition, VCH Ed., 1997, pp. 300-301), the allyl alcohol possibly being obtained by alkaline hydrolysis of allyl chloride, 10 or by isomerization of propylene oxide, or by hydrogenation of acrolein or by hydrolysis of allyl acetate, these various compounds being themselves obtained starting from propylene. Such routes are not very environmentally friendly, as in such processes the glycidol is obtained from propylene, itself deriving from a non-renewable raw material, oil, gas or coal.

15 The object of the present invention is to provide a process for manufacturing glycidol which does not have these disadvantages.

The invention hence relates to a process for manufacturing glycidol comprising at least the following steps:

- a) glycerol and a chlorinating agent are reacted to form monochloropropanediol 20 in a first reaction medium; and
- b) at least one basic compound is reacted with at least one part of the first reaction medium from step a) to form glycidol and a salt in a second reaction medium, the organic component of which has a monochloropropanediol content before reaction with the basic compound greater than 100 g/kg of 25 organic component.

It has been discovered that when proceeding in this manner, it is possible, *inter alia*, to use reactants which may be obtained from renewable raw materials.

In the rest of the document, and except where otherwise mentioned, the expressions "reaction medium from step a)", "first reaction medium" and "first 30 reaction medium from step a)" will be equivalent and the expressions "reaction medium from step b)", "second reaction medium" and "second reaction medium from step b)" will be equivalent.

5 The reaction medium from step a) may especially contain glycerol, a chlorinating agent, a carboxylic acid, a solvent, dichloropropanol, a salt, water and by-products from the glycerol chlorination reaction, as described in Application WO 2006/100314 by Solvay SA, of which the content, and more specifically, the passage from page 13, line 35 to page 15, line 18, is incorporated here by reference. The composition of the reaction medium from step a) may develop in the course of the reaction from step a). Thus, glycerol for example may be absent from the reaction medium from step a) at the end of this step.

10 Step a) may be carried out in batch or continuous mode, preferably in continuous mode.

The reaction from step a) is carried out at a temperature generally greater than or equal to 20°C, usually greater than or equal to 30°C, commonly greater than or equal to 40°C, in many cases greater than or equal to 60°C, often greater than or equal to 80°C, and frequently greater than or equal to 90°C. This temperature is generally less than or equal to 300°C, generally less than or equal to 250°C, commonly less than or equal to 200°C, in many cases less than or equal to 180°C, often less than or equal to 160°C, and frequently less than or equal to 140°C.

20 The reaction from step a) is carried out at a pressure generally greater than or equal to 0.3 bar absolute, usually greater than or equal to 0.5 bar absolute and commonly greater than or equal to 1 bar absolute. This pressure is generally less than or equal to 100 bar absolute, usually less than or equal to 20 bar absolute, commonly less than or equal to 15 bar absolute and in many cases less than or equal to 10 bar absolute.

25 When step a) is carried out in batch mode, the reaction from step a) is carried out over a duration generally greater than or equal to 0.5 h, usually greater than or equal to 2 h and commonly greater than or equal to 5 h. This duration is generally less than or equal to 20 h, usually less than or equal to 15 h and commonly less than or equal to 10 h.

30 When step a) is carried out in continuous mode, the reaction from step a) is carried out for a residence time generally greater than or equal to 1 h, usually greater than or equal to 2 h and commonly greater than or equal to 5 h. This residence time is generally less than or equal to 50 h, usually less than or equal to 20 h and commonly less than or equal to 10 h.

In step a) of the process according to the invention, glycerol may be obtained starting from fossil raw materials and/or renewable raw materials, as described in Application WO 2005/054167 by Solvay SA, of which the content, and more specifically the passage from page 1, line 26 to page 4, line 2, is
5 incorporated here by reference, as described in Application WO 2006/100312 by Solvay SA, of which the content, and more specifically the passage from page 3, line 29 to page 5, line 24, is incorporated here by reference, and as described in Application FR 07/56125 by Solvay SA, of which the content, and more specifically the passage from page 4, line 35 to page 5, line 22, is incorporated
10 here by reference.

In step a) of the process according to the invention, glycerol may have a content of alkali and/or alkaline-earth metals such as described in Application WO 2006/100315 by Solvay SA, of which the content, and more specifically the passage from page 7, line 11 to page 9, line 10, is incorporated here by reference.

15 In step a) of the process according to the invention, glycerol may contain elements other than the alkali and alkaline-earth metals such as described in Application WO 2006/100319 by Solvay SA, of which the content, and more specifically the passages from page 2, lines 3 to 8 and from page 6, line 20 to page 9, line 14, is incorporated here by reference.

20 In step a) of the process according to the invention, glycerol generally contains an amount of heavy compounds other than glycerol such as described in Application WO 2006/100319 by Solvay SA, of which the content, and more specifically the passage from page 9, line 15 to page 10, line 15, is incorporated here by reference.

25 In the process according to the invention, glycerol may contain glycerol alkyl ethers as described in Application PCT/EP2007/055742 by Solvay SA, of which the content, and more specifically the passage from page 1, line 23 to page 3, line 25, is incorporated here by reference.

30 In the process according to the invention, glycerol may contain diols as described in Application FR 07/56125 by Solvay SA, of which the content, and more specifically the passage from page 1, line 17 to page 3, line 5, is incorporated here by reference.

35 In step a) of the process according to the invention, the chlorinating agent generally comprises hydrogen chloride. The hydrogen chloride may be in the form of optionally anhydrous gas or of an aqueous solution of hydrogen chloride or a mixture of the two, preferably in the form of gas or a mixture of gas and an

aqueous solution of hydrogen chloride. The chlorinating agent may at least partly come from processes such as described in Application WO 2005/054167 by Solvay SA, of which the content, and more specifically the passage from page 4, line 32 to page 5, line 18, is incorporated here by reference, such as

5 described in Application WO 2006/106153, of which the content, and more specifically the passage from page 2, line 10 to page 3, line 20, is incorporated here by reference, and such as described in Application EP 2007/055742 by Solvay SA, of which the content, and more specifically the passage from page 12, line 34 to page 13, line 35, is incorporated here by reference.

10 In step a) of the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out in a reactor such as described in Application WO 2005/054167 by Solvay SA, of which the content, and more specifically the passage from page 6, lines 3 to 33, is incorporated here by reference, and in equipment produced from or covered with materials that are

15 resistant to the chlorinating agent, such as described in Application WO 2006/100317 by Solvay SA, of which the content, and more specifically the passages from page 2, line 29 to page 3, line 7 and from page 23, line 22 to page 27, line 25, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between

20 glycerol and the chlorinating agent may be carried out in a reaction medium such as described in Application WO 2006/106154 by Solvay SA, of which the content, and more specifically the passage from page 14, line 15 to page 17, line 10, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between

25 glycerol and the chlorinating agent may be carried out in the presence of a catalyst such as described in Application WO 2005/054167 by Solvay SA, of which the content, and more specifically the passage from page 6, line 24 to page 7, line 35, is incorporated here by reference, and in Application WO 2006/020234, of which the content, and more specifically the passage from page

30 12, line 20 to page 18, line 3, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out at a catalyst concentration, at a temperature, at a pressure and for a residence time such as described in Application WO 2005/054167 by Solvay SA, of which the content, and more

35 specifically the passage from page 8, line 1 to page 10, line 10, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out as described in Application WO 2007/054505 by Solvay SA, of which the content, and more specifically the passages from page 1, lines 24 to 31 and from page 2, line 6 to
5 page 6, line 18, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out in the presence of a solvent such as described in Application WO 2005/054167 by Solvay SA, of which the content, and more specifically the passage from page 11, lines 12 to
10 36, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out in the presence of a liquid phase comprising heavy compounds other than glycerol as described in Application WO 2006/100316 by Solvay SA, of which the content, and more
15 specifically the passages from page 2, lines 18 to 20 and from page 17, line 12 to page 19, line 9, is incorporated here by reference.

In step a) of the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out with stirring using a stirring system such as described in Application EP 07109461.9 by Solvay SA,
20 of which the content, and more specifically the passages from page 1, lines 26 to 32 and from page 5, line 15 to page 10, line 22, is incorporated here by reference.

In the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out in a liquid reaction medium such as described in Application WO 2006/100319 in the name of Solvay SA, of which
25 the content, and more specifically the passages from page 2, lines 3 to 8 and from page 17, line 12 to page 19, line 9, is incorporated here by reference.

In the process according to the invention, the reaction between glycerol and the chlorinating agent may be carried out in a reactor, the supply of which is such as described in Application FR 07/53689 in the name of Solvay SA, of
30 which the content, and more specifically the passage from page 1, line 26 to page 4, line 13, is incorporated here by reference.

The reaction medium from step b) is defined as the medium where the reaction between monochloropropanediol and the basic compound occurs. This medium comprises the compounds necessary for the reaction from step b),
35 among which are monochloropropanediol and the basic compound. The reaction medium from step b) comprises an organic component, usually an organic

component and an inorganic component. This reaction medium is generally constituted of an organic component and an inorganic component. The organic component is constituted of all the organic compounds of the reaction medium that are solid, liquid or gaseous, dissolved or dispersed, at the reaction
5 temperature and pressure. The organic compounds are compounds of which the molecule comprises at least one carbon-hydrogen bond or one carbon-carbon bond. The inorganic component is composed of all the inorganic compounds of the reaction medium that are solid, liquid or gaseous, dissolved or dispersed, at the reaction temperature. The reaction medium from step b) may be single phase
10 or multiphase. The reaction medium from step b) often comprises a single liquid phase.

The monochloropropanediol may be 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol or a mixture of these two isomers. The 3-chloro-1,2-propanediol content is usually greater than or equal to 500 g/kg of mixture of
15 these two isomers, generally greater than or equal to 750 g/kg and commonly greater than or equal to 900 g/kg. Monochloropropanediol essentially composed of 3-chloro-1,2-propanediol is particularly suitable.

The monochloropropanediol content in the organic component of the reaction medium from step b) before reaction with the basic compound is greater
20 than or equal to 100 g/kg of organic component, often greater than or equal to 400 g/kg, frequently greater than or equal to 750 g/kg, especially greater than or equal to 900 g/kg, in particular greater than or equal to 950 g/kg and specifically greater than or equal to 990 g/kg.

In step b) of the process for manufacturing glycidol according to the
25 invention, at least one part of the monochloropropanediol is obtained by reaction between glycerol and a chlorinating agent. Another part may be obtained by hydrolysis of epichlorohydrin. The latter reaction may be a secondary reaction of an epichlorohydrin manufacturing process, such as dehydrochlorination of dichloropropanol and/or epoxidation of allyl chloride.

In step b) of the process according to the invention, the proportion of
30 monochloropropanediol which comes from a reaction other than the reaction between glycerol and a chlorinating agent is generally less than or equal to 90 wt% of monochloropropanediol, usually less than or equal to 50 wt%, commonly less than or equal to 25 wt%, in many cases less than or equal to
35 10 wt%, often less than or equal to 5 wt%, and frequently less than or equal to 1 wt%. Monochloropropanediol essentially derived from a glycerol chlorination

process is particularly suitable. Such a process is described in Patent Application WO 2005/054167 by Solvay SA, of which the content is incorporated here by reference.

In step b) of the process according to the invention, the
5 monochloropropanediol may be extrinsic monochloropropanediol, recycled monochloropropanediol or a mixture of the two. The expression "recycled monochloropropanediol" is understood to mean monochloropropanediol which has been separated in a step subsequent to step b) in the process according to the invention and which has then been recycled to step b) of said process. The
10 expression "extrinsic monochloropropanediol" is understood to mean monochloropropanediol that has not been recycled.

In step b) of the process according to the invention, the extrinsic monochloropropanediol content in the monochloropropanediol is generally at least 40 wt%, usually at least 80 wt%, commonly at least 90 wt% and in many
15 cases at least 95 wt%. A monochloropropanediol essentially composed of extrinsic monochloropropanediol is very suitable.

In the process according to the invention, the reaction medium from step b) may contain water. The water may be introduced with the monochloropropanediol. In this case, the water content introduced by the
20 monochloropropanediol relative to the sum of the water content introduced by the monochloropropanediol and the monochloropropanediol content is generally greater than or equal to 5 g of water/kg, usually greater than or equal to 20 g/kg and frequently greater than or equal to 50 g/kg. This water content is generally less than or equal to 850 g/kg.

In the process according to the invention, the reaction medium from step b) may also contain carboxylic acids. These acids may be introduced with the monochloropropanediol. These acids may be catalysts for the reaction between glycerol and a chlorinating agent such as those mentioned above. In this case, the content of carboxylic acids introduced by the monochloropropanediol
30 relative to the sum of the content of carboxylic acids introduced by the monochloropropanediol and the monochloropropanediol content is generally less than 10 mol%, usually less than 3 mol%, commonly less than 0.1 mol% and often less than 0.001 mol%.

In the process according to the invention, the reaction medium from step b)
35 may also contain mineral acids such as, for example, hydrogen chloride. These acids may be introduced by the monochloropropanediol. The hydrogen chloride

content relative to the sum of the hydrogen chloride content introduced by the monochloropropanediol and the monochloropropanediol content is generally less than or equal to 50 wt%, usually less than or equal to 25 wt%, commonly less than or equal to 2 wt% and in many cases less than or equal to 0.01 wt%.

5 In the process according to the invention, the reaction medium from step b) may also contain organic compounds other than the monochloropropanediol and carboxylic acids. These organic compounds may, for example, be derived from the monochloropropanediol synthesis process. They may be, for example, glycerol, glycerol esters, monochloropropanediol esters, dichloropropanol, 10 dichloropropanol esters, partially chlorinated and/or esterified glycerol oligomers, aldehydes, acrolein, 1-chloroacetone, linear or cyclic, usually cyclic chloroethers and commonly cyclic ethers of crude chemical formula $C_6H_{10}O_2Cl_2$, and any mixtures of at least two of them. The content of these other organic compounds relative to the sum of the contents of these organic compounds 15 introduced by monochloropropanediol and the monochloropropanediol content is generally less than or equal to 100 g/kg, usually less than or equal to 50 g/kg and commonly less than or equal to 20 g/kg. The content of dichloropropanol relative to the sum of the content of dichloropropanol introduced by monochloropropanediol and the monochloropropanediol content is generally less 20 than or equal to 100 g/kg, usually less than or equal to 50 g/kg and commonly less than or equal to 20 g/kg, in many cases less than or equal to 10 g/kg, often less than or equal to 5 g/kg, frequently less than or equal to 1 g/kg and in particular less than or equal to 0.1 g/kg. That content is usually higher than or equal to 0.01 g/kg.

25 In step b) of the process according to the invention, the basic compound may be such as described in Application FR 07/53375 in the name of Solvay SA, of which the content, and more specifically the passage from page 6, line 7 to page 7, line 33, is incorporated here by reference.

30 In the process according to the invention, the water content of the reaction medium from step b) is generally less than or equal to 950 g/kg of reaction medium, usually less than or equal to 800 g/kg and commonly less than or equal to 700 g/kg. This water content is generally greater than or equal to 100 g/kg of reaction medium, usually greater than 200 g/kg and commonly greater than 350 g/kg.

35 In a first way of proceeding according to the invention, in step b), the monochloropropanediol is used in stoichiometric or substoichiometric amounts

with respect to the effective amount of the basic compound. The expression "effective amount of the basic compound" is understood to mean the amount of basic compound reduced to the amount required for the reaction with the organic and mineral acids optionally present in the reaction medium. In this case, at least 1 effective equivalent of the basic compound per equivalent of monochloropropanediol needed to form glycidol is generally used. At least 1.2 effective equivalents of basic compound are usually used and at least 1.5 effective equivalents of basic compound are frequently used and at most 5 effective equivalents of basic compound are generally used.

In a second way of proceeding according to the invention, which is preferred, in step b), the monochloropropanediol is used in excess with respect to the effective amount of the basic compound. In this case, at least 0.99 effective equivalent of basic compound per equivalent of monochloropropanediol needed to form glycidol is generally used. At most 0.95 effective equivalent of basic compound is usually used, at most 0.8 effective equivalent of basic compound is frequently used and at a minimum 0.2 effective equivalent of basic compound is used. The advantage of working with a deficit of basic compound per equivalent of monochloropropanediol is making it possible to reduce the glycidol degradation reactions (especially the hydrolysis reactions) during step b).

When dichloropropanol is present in the reaction medium from step b), the effective equivalents of basic compound mentioned above are relative to the sum of the equivalents of monochloropropanediol and of dichloropropanol needed to form, respectively, glycidol and epichlorohydrin.

The reaction medium from step b) may contain an organic solvent. All organic substances that dissolve glycidol and that are not, or not very, miscible with water may be used as solvent. The expression "organic substances that are not, or not very, miscible with water" is understood to mean organic substances whose solubility in water at 25 °C is at most 50 g/kg. These substances may, for example, be dichloropropanol and/or epichlorohydrin. The solvent content of the reaction medium relative to the organic component of the reaction medium is generally less than or equal to 80 wt%, usually less than or equal to 50 wt%, commonly less than or equal to 30 wt% and in many cases less than or equal to 10 wt%. Most particularly preferably, the reaction medium from step b) does not contain an organic solvent, other than dichloropropanol and/or epichlorohydrin.

Step b) of the process according to the invention may be carried out in batch, semi-continuous or continuous mode. The continuous mode, in which the reaction medium is continuously supplied and drawn off, is preferred.

5 In the process according to the invention, the salt formed in step b) may be an organic salt, an inorganic salt or a mixture of the two. The salt is preferably an inorganic salt and more preferably a salt chosen from alkali and alkaline-earth metal chlorides, sulphates, hydrogensulphates, hydroxides, carbonates, hydrogencarbonates, phosphates, hydrogenphosphates and borates, and mixtures thereof. A portion of these salts cannot be produced in the course of the reaction
10 between monochloropropanediol and the basic compound during step b) of the process according to the invention. These salts may thus be present, for example, in the monochloropropanediol and the basic compound. These salts may also be present in and/or added to step a) and/or step b) of the process according to the invention. Preferably, these salts are partly formed in the
15 reaction from step b) and are partly present in the basic compound.

In the process for manufacturing glycidol according to the invention, the reaction from step b) is generally carried out at a temperature, under a pressure, for a duration or a residence time, with stirring, in a reactor and according to a method such as described for step a) of the process claimed in Application
20 FR 07/53375 by Solvay SA, of which the content, and more specifically the passage from page 9, line 6 to page 10, line 18, is incorporated here by reference.

The process according to the invention may comprise at least one supplementary step c) in which at least one part of the second reaction medium obtained at the end of step b) is subjected to at least one treatment chosen from
25 settling and liquid/liquid extraction operations, alone or in combination, at the end of which treatment a first fraction containing most of the glycidol which was contained in the part of the second reaction medium from step b) before said treatment from step c) and a second fraction containing most of the salt which was contained in the part of the second reaction medium from step b) before said
30 treatment from step c) are separated.

In a first embodiment of the process according to the invention, the treatment from step c) comprises at least one settling operation.

This treatment is generally used when the reaction medium obtained at the end of step b) comprises at least two liquid phases. This scenario may be
35 encountered, for example, when the reaction medium from step b) contains an organic solvent such as defined above and/or the dichloropropanol, and

preferably 2,3-dichloro-1-propanol, content relative to the sum of the monochloropropanediol and dichloropropanol contents in the reaction medium from step b) before reaction with the basic compound is high.

In the first embodiment of the process according to the invention, the settling operation from step c) may be carried out by gravity or by centrifugation. Settling by gravity is preferred.

In the process according to the invention, the settling operation from step c) may be carried out at a temperature, under a pressure, for a duration or a residence time and according to a method such as described for step b) of the manufacturing process claimed in Application FR 07/53375 in the name of Solvay SA, of which the content, and more specifically the passage from page 10, line 19 to page 11, line 9, is incorporated here by reference.

In a second embodiment of the process according to the invention, which is preferred, the treatment from step c) comprises at least one liquid/liquid extraction operation. This treatment is generally used when the reaction medium obtained at the end of step b) comprises a single liquid phase. This scenario may be encountered when the reaction medium from step b) does not contain an organic solvent such as defined above or when the dichloropropanol content relative to the sum of the monochloropropanediol and dichloropropanol contents in the reaction medium from step b) before reaction with the basic compound is low.

The extraction solvent is generally such as described in Application FR 07/55697 by Solvay SA, of which the content, and more specifically the passage from page 10, line 23 to page 13, line 12, is incorporated here by reference.

The extraction solvent is generally an organic solvent which may be chosen from epoxides other than glycidol, esters, ketones, ethers, alcohols, carboxylic acids, organic phosphates and phosphine oxides. The organic solvents may contain water, preferably up to saturation.

Dichloropropanol, epichlorohydrin and mixtures thereof are particularly preferred extraction solvents.

The liquid/liquid extraction operation is generally carried out at a temperature and under a pressure such as described in Application FR 07/55697 by Solvay SA, of which the content, and more specifically the passage from page 13, lines 13 to 23, is incorporated here by reference.

In these various embodiments, the part of the reaction medium at the end of step b) may be subjected to a treatment prior to those of step c). This treatment may be such as described in Application FR 07/53375 by Solvay SA, of which the content, and more specifically the passage from page 3, lines 1 to 21, is incorporated here by reference.

At the end of the treatment from step c) of the process according to the invention, it is also possible to separate a third fraction, as described in Application FR 07/53375 by Solvay SA, of which the content, and more specifically the passage from page 19, lines 12 to 25, is incorporated here by reference.

In these various embodiments of the process according to the invention, recovered at the end of the treatment from step c) is a first fraction containing most of the glycidol which was contained in the part of the reaction medium obtained at the end of step b) before the treatment from step c), and light products, that is to say of which the boiling point under a pressure of 1 bar absolute is below the boiling point of glycidol, such as acetaldehyde, acrolein, water, 1,3-dichloropropene, epichlorohydrin, methyl glycidyl ether, chloroacetone, 1,3-dichloropropane, 2-chloroethanol, cyclopentanone, 2-chloro-2-propen-1-ol, hydroxyacetone, 1,2,3-trichloropropane, and 2-methyl-2-cyclopenten-1-one, heavy products, that is to say of which the boiling point under a pressure of 1 bar absolute is above the boiling point of glycidol such as 3-chloro-1-propanol, 1,3-dichloropropan-2-ol, chloropropanol, 2,3-dichloropropan-1-ol, 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol and partially chlorinated and/or esterified glycerol oligomers.

The proportion of glycidol present in the part of the reaction medium obtained at the end of step b) of the process according to the invention and before the treatment from step c), which is found in the first fraction separated at the end of step c), is generally at least 80%, usually at least 90% and commonly at least 95%.

The first fraction recovered at the end of the treatment from step c) contains glycidol in an amount generally greater than or equal to 50 g of glycidol/kg of first fraction, usually greater than or equal to 100 g/kg, commonly greater than or equal to 200 g/kg, in many cases greater than or equal to 300 g/kg and often greater than or equal to 400 g/kg. The glycidol content of the first fraction separated is generally less than or equal to 500 g/kg. The glycidol content of the first fraction separated depends, for example, on the use of an

organic solvent and/or on an incomplete conversion of the mixture of 3-chloro-1,2-propanediol and 2-chloro-1,3-propanediol.

The first fraction separated at the end of the treatment from step c) contains chloroacetone in an amount generally less than or equal to 2 g of

5 chloroacetone/kg of first fraction and usually less than or equal to 0.3 g/kg, commonly less than or equal to 0.1 g/kg, and in many cases less than or equal to 0.05 g/kg. The chloroacetone content is generally greater than or equal to 0.005 g/kg.

10 The first fraction separated at the end of the treatment from step c) contains acrolein in an amount generally less than or equal to 5 g of acrolein/kg of first fraction and usually less than or equal to 0.3 g/kg and commonly less than or equal to 0.1 g/kg. The acrolein content is generally greater than or equal to 0.07 g/kg.

15 The first fraction separated at the end of the treatment from step c) contains chloroethers in an amount generally less than or equal to 20 g of chloroethers/kg of first fraction, usually less than or equal to 5 g/kg, commonly less than or equal to 2 g/kg, and in many cases less than or equal to 1 g/kg. The content of chloroethers is generally greater than or equal to 0.5 g/kg.

20 Chloroethers are compounds of which the molecule comprises at least one chlorine atom and at least one oxygen atom, this oxygen atom being bonded to two carbon atoms. Epichlorohydrin is not considered here as a chloroether. These chloroethers preferably contain six carbon atoms. These chloroethers preferably contain two, sometimes three, chlorine atoms. These chloroethers preferably contain two oxygen atoms. These chloroethers are usually chosen
25 from compounds of crude chemical formula: $C_6H_{10}Cl_2O_2$, $C_6H_{12}Cl_2O$, $C_6H_9Cl_3O_2$, $C_6H_{11}Cl_3O_2$, $C_6H_{13}ClO_4$ and $C_6H_{12}Cl_2O_3$ and mixtures of at least two of them.

The first fraction separated at the end of the treatment from step c) contains the chloroether of crude chemical formula $C_6H_{10}Cl_2O_2$ in an amount generally
30 less than or equal to 50 g of chloroether of crude chemical formula $C_6H_{10}Cl_2O_2$ /kg of first fraction, usually less than or equal to 10 g/kg, commonly less than or equal to 0.5 g/kg, and in many cases less than or equal to 0.1 g/kg. The content of this chloroether is generally greater than or equal to 0.05 g/kg.

35 The first fraction separated at the end of the treatment from step c) contains the chloroether of crude formula $C_6H_{12}Cl_2O$ in an amount generally less than or equal to 5 g of chloroether of crude chemical formula $C_6H_{12}Cl_2O$ /kg of first

fraction, usually less than or equal to 2 g/kg, commonly less than or equal to 0.5 g/kg, and in many cases less than or equal to 0.1 g/kg. The content of this chloroether is generally greater than or equal to 0.05 g/kg.

5 The first fraction separated at the end of the treatment from step c) contains the chloroether of crude chemical formula $C_6H_9Cl_3O_2$ in an amount generally less than or equal to 5 g of chloroether of crude chemical formula $C_6H_9Cl_3O_2$ /kg of first fraction, usually 2 g/kg, commonly less than or equal to 0.5 g/kg, and in many cases less than or equal to 0.1 g/kg. The content of this chloroether is generally greater than or equal to 0.02 g/kg.

10 The first fraction separated at the end of the treatment from step c) contains the chloroether of crude chemical formula $C_6H_{11}Cl_3O_2$ in an amount generally less than or equal to 5 g of chloroether of crude chemical formula $C_6H_{11}Cl_3O_2$ /kg of first fraction, usually at most 2 g/kg, commonly less than or equal to 1 g/kg, and in many cases less than or equal to 0.6 g/kg. The content of this chloroether is generally greater than or equal to 0.5 g/kg.

15 The first fraction separated at the end of the treatment from step c) contains the chloroether of crude chemical formula $C_6H_{12}Cl_2O_3$ in an amount generally less than or equal to 50 g of chloroether of crude chemical formula $C_6H_{12}Cl_2O_3$ /kg of first fraction, usually less than or equal to 20 g/kg, commonly less than or equal to 1 g/kg, and in many cases less than or equal to 0.6 g/kg. The content of this chloroether is generally greater than or equal to 0.5 g/kg.

20 The first fraction separated at the end of the treatment from step c) contains the chloroether of crude chemical formula $C_6H_{13}ClO_4$ in an amount generally less than or equal to 50 g of chloroether of crude chemical formula $C_6H_{13}ClO_4$ /kg of first fraction, usually less than or equal to 20 g/kg, commonly less than or equal to 1 g/kg, and in many cases less than or equal to 0.6 g/kg. The content of this chloroether is generally greater than or equal to 0.5 g/kg.

25 The first fraction separated at the end of the treatment from step c) generally contains other organic compounds such as, for example, 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol and mixtures thereof. The sum of the contents of these monochloropropanediols is generally less than or equal to 900 g/kg of first fraction, usually less than or equal to 800 g/kg, commonly less than or equal to 700 g/kg, in many cases less than or equal to 500 g/kg, often less than or equal to 300 g/kg and frequently less than or equal to 200 g/kg. The sum of the contents of these monochloropropanediols is generally greater than or equal to 10 g/kg.

The sum of the glycerol, hydroxyacetone and epichlorohydrin contents is generally less than or equal to 100 g/kg of first fraction, frequently less than or equal to 50 g/kg, usually less than or equal to 30 g/kg, in particular less than or equal to 10 g/kg and more specifically less than or equal to 1 g/kg. The sum of these contents is generally greater than or equal to 0.1 g/kg.

The sum of the 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol contents is generally less than or equal to 5 g/kg of first fraction, usually less than or equal to 3 g/kg, commonly less than or equal to 1 g/kg. This sum is generally greater than or equal to 0.5 g/kg.

The methyl glycidyl ether content is generally less than or equal to 5 g/kg of first fraction, usually less than or equal to 3 g/kg and commonly less than or equal to 1 g/kg. This content is generally greater than or equal to 0.005 g/kg.

The 1,2,3-trichloropropane content is generally less than or equal to 10 g/kg of first fraction, usually less than or equal to 5 g/kg, commonly less than or equal to 3 g/kg and in many cases less than or equal to 1 g/kg. This content is generally greater than or equal to 0.01 g/kg.

The sum of the contents of cis- and trans-1,3-dichloropropenes is generally less than or equal to 2 g/kg of first fraction, usually less than or equal to 1 g/kg, and commonly less than or equal to 0.1 g/kg. This sum is generally greater than or equal to 0.01 g/kg.

The 1,3-dichloropropane content is generally less than or equal to 2 g/kg of first fraction, preferably less than or equal to 1 g/kg, and usually less than or equal to 0.5 g/kg. This content is generally greater than or equal to 0.01 g/kg.

The 2-chloro-2-propen-1-ol content is generally less than or equal to 2 g/kg of first fraction, usually less than or equal to 1 g/kg, and commonly less than or equal to 0.5 g/kg. This content is generally greater than or equal to 0.01 g/kg.

The first fraction separated at the end of the treatment from step c) generally contains water and inorganic compounds such as the basic compound and the salt, in particular the basic compounds and the salts as defined above.

The water content is generally less than or equal to 90 g/kg of first fraction, frequently less than or equal to 80 g/kg, usually less than or equal to 50 g/kg, more specifically less than or equal to 30 g/kg and even more specifically less than or equal to 15 g/kg. The water content is generally greater than or equal to 1 g/kg of first fraction.

The salt content is generally less than or equal to 10 g/kg of first fraction, frequently less than or equal to 5 g/kg, usually less than or equal to 2 g/kg, more specifically less than or equal to 0.1 g/kg and even more specifically less than or equal to 0.015 g/kg. This salt content is generally greater than or equal to
5 0.01 g/kg.

The first fraction recovered at the end of the treatment from step c) may be used as a stabilizer in natural oils and vinyl polymers, as a reaction intermediate in the manufacture of glycerol, glycidyl ethers, glyceryl ethers, esters and amines, as a reactant in processes for manufacturing functionalized epoxides
10 such as 2,3-epoxypropyloxy chloroformate and 2,3-epoxypropyl urethanes, as an alkylating agent, as an anti-emulsifier and for stabilizing milk of magnesia.

The invention also relates to an organic composition of which the glycidol content is greater than or equal to 100 g/kg of organic composition and of which the 3-chloro-1-propanol content is greater than or equal to 0.005 g/kg and less
15 than or equal to 2 g/kg of organic composition, the organic composition possibly being obtained according to the process described above, in which case the first fraction separated at the end of the treatment from step c) constitutes the organic composition.

The invention also relates to the use of this organic composition as a
20 stabilizer in natural oils and vinyl polymers, as a reaction intermediate in the manufacture of glycerol, glycidyl ethers, glyceryl ethers, esters and amines, as a reactant in processes for manufacturing functionalized epoxides such as 2,3-epoxypropyloxy chloroformate and 2,3-epoxypropyl urethanes, as an alkylating agent, as an anti-emulsifier and for stabilizing milk of magnesia.

This first fraction may be subjected to supplementary treatments similar to those described in Application FR 07/55696 filed in the name of Solvay SA and of which the content, and more specifically the passage from page 10, line 30 to page 16, line 33, is incorporated here by reference, and which comprise dilution, concentration, evaporation, distillation, stripping, liquid/liquid extraction and
25 adsorption operations, alone or in combination, so as to separate the glycidol, other organic compounds and optionally the extraction solvent, and to obtain a purified glycidol-based product.

This purified glycidol-based product contains glycidol in an amount greater than or equal to 900 g of glycidol per kg of product, preferably greater
35 than or equal to 950 g/kg, more preferably greater than or equal to 990 g/kg and

most particularly preferably at least 999 g/kg, and at least one halogenated hydrocarbon in an amount less than or equal to 1 g/kg of product.

The halogenated hydrocarbon may be an aliphatic or aromatic halogenated hydrocarbon, optionally containing oxygen, preferably an aliphatic halogenated hydrocarbon, such as trichloropropane, preferably 1,2,3-trichloropropane, 5 chloropropenol, preferably 2-chloro-2-propen-1-ol, dichloropropene, preferably cis-1,3-dichloropropene, trans-1,3-dichloropropene, and mixtures thereof, dichloropropane, preferably 1,3-dichloropropane, dichloropropanol, preferably 1,3-dichloropropan-2-ol, 2,3-dichloropropan-1-ol, and mixtures thereof, 10 monochloropropanediol, preferably 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol, and mixtures thereof, and chloroethers, preferably chosen from chloroethers of crude formula: $C_6H_{10}Cl_2O_2$, $C_6H_{12}Cl_2O$, $C_6H_9Cl_3O_2$, $C_6H_{11}Cl_3O_2$, $C_6H_{13}ClO_4$, a halogenated ketone such as 1-chloroacetone, epichlorohydrin and mixtures of at least two of them.

15 The invention also relates to the use of this purified glycidol-based product as a stabilizer in natural oils and vinyl polymers, as a reaction intermediate in the manufacture of glycerol, glycidyl ethers, glyceryl ethers, esters and amines, as a reactant in processes for manufacturing functionalized epoxides such as 2,3-epoxypropyloxy chloroformate and 2,3-epoxypropyl urethanes, as an alkylating 20 agent, as an anti-emulsifier and for stabilizing milk of magnesia.

In these various embodiments of the process according to the invention, recovered at the end of the treatment from step c) is a second fraction which contains most of the salt which was contained in the part of the reaction medium obtained at the end of step b) before the treatment from step c).

25 In the process for manufacturing glycidol according to the invention, the salt included in the second fraction separated in step c) may be an organic or inorganic salt as defined above. Inorganic salts are preferred. The expression "inorganic salts" is understood to mean salts whose constituent ions do not contain a carbon-hydrogen bond or a carbon-carbon bond.

30 In the process for manufacturing glycidol according to the invention, the second fraction separated at the end of the treatment from step c) generally comprises water. The water content is generally greater than or equal to 500 g of water per kg of second fraction, usually greater than or equal to 600 g/kg, commonly greater than or equal to 700 g/kg and in many cases greater than or 35 equal to 750 g/kg. The water content is generally less than or equal to 990 g of water per kg of second fraction, usually less than or equal to 950 g/kg,

commonly less than or equal to 900 g/kg and in many cases less than or equal to 850 g/kg.

5 The proportion of salt present in the part of the reaction medium obtained at the end of step b) of the process according to the invention and before the treatment from step c), which is found in the second fraction separated in step c), is generally greater than or equal to 80%, usually greater than or equal to 90% and commonly greater than or equal to 95%.

10 In the process for manufacturing glycidol according to the invention, the second fraction separated at the end of the treatment from step c) comprises a salt in an amount generally greater than or equal to 50 g of salt/kg, usually greater than or equal to 100 g of salt/kg, commonly greater than or equal to 150 g of salt/kg and in many cases greater than or equal to 200 g of salt/kg. Most particularly, the salt concentration is below the solubility limit of the salt in this second fraction.

15 The advantage of a salt content at the limit of its solubility in the second fraction separated at the end of the treatment from step c) is two-fold. It makes it possible, on the one hand, to reduce the concentration of organic compounds in the second fraction (salting-out effect) and, on the other hand, to reduce the water content of the first fraction.

20 The salts present in the second fraction separated at the end of the treatment from step c) of the process according to the invention are such as mentioned above. A portion of these salts cannot be produced in the course of the reaction between the monochloropropanediol and the basic agent during step b) of the process according to the invention. These salts may thus be present in the reactants, for example in the monochloropropanediol and the basic
25 compound. The salts may also be added to step b) and/or to step c) of the process according to the invention, for example before the settling or liquid/liquid extraction operation. Preferably, these salts are partly formed in the reaction from step b) and are partly present in the basic compound.

30 In the process according to the invention, the second fraction may contain organic compounds. The latter may come from the monochloropropanol manufacturing process and/or be formed during the reaction between the monochloropropanol and the basic compound during step b) of the process according to the invention. Examples of these compounds are glycidol,
35 1,3-dichloro-2-propanol, 2,3-dichloro-1-propanol, glycerol, 3-chloro-1,2-

propanediol, 2-chloro-1,3-propanediol, chloroacetone, hydroxyacetone, epichlorohydrin and 2-chloro-2-propen-1-ol.

5 The glycidol content of the second fraction separated at the end of the treatment from step c) is generally greater than or equal to 0.1 g/kg of second fraction, usually greater than or equal to 1 g/kg, commonly greater than or equal to 5 g/kg and in many cases greater than or equal to 10 g/kg. This content is generally less than or equal to 60 g/kg, usually less than or equal to 50 g/kg, commonly less than or equal to 40 g/kg and in many cases less than or equal to 35 g/kg.

10 The sum of the 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol contents in the second fraction separated at the end of the treatment from step c) is generally greater than or equal to 0.01 g/kg of second fraction, usually greater than or equal to 1 g/kg and commonly greater than or equal to 2 g/kg. This sum is generally less than or equal to 100 g/kg, usually less than or equal to 80 g/kg and commonly less than or equal to 40 g/kg.

15 The sum of the 3-chloro-1,2-propanediol and 2-chloro-1,3-propanediol contents in the second fraction separated at the end of the treatment from step b) is generally less than or equal to 50 g/kg of second fraction, usually less than or equal to 10 g/kg and commonly less than or equal to 1 g/kg. This sum is generally greater than or equal to 0.1 g/kg.

20 In the process according to the invention, the second fraction separated may contain a basic compound such as defined above, preferably an inorganic basic compound. This inorganic basic compound may be chosen from alkali or alkaline-earth metal oxides, hydroxides, carbonates, hydrogencarbonates, phosphates, hydrogenphosphates and borates, and mixtures of at least two of them. The inorganic basic compound content is generally greater than or equal to 0.1 g/kg of second fraction, usually greater than or equal to 0.5 g/kg and commonly greater than or equal to 1 g/kg. This content is generally less than or equal to 25 g/kg of second fraction, usually less than or equal to 10 g/kg and commonly less than or equal to 5 g/kg.

30 The total organic carbon (TOC) content of the second fraction separated at the end of the treatment from step c) is generally less than or equal to 40 g of carbon/kg of second fraction separated in step b) and frequently less than or equal to 16 g/kg and usually less than or equal to 13 g/kg.

35 The second fraction separated at the end of the treatment from step c) may be conveyed as is to an electrolysis process. The electrolysis process is, for

example, a process for producing chlorine and sodium hydroxide, when the inorganic salt is sodium chloride, for example.

The sodium hydroxide produced in such a process may advantageously be recycled to step a) of the process according to the invention.

5 The chlorine produced in such a process may advantageously be used in a hydrochloric acid manufacture, by direct synthesis with hydrogen for example, or in a manufacture of which the hydrochloric acid is one of the co-products, such as manufacture of allyl chloride by chlorination of propylene for example. This hydrochloric acid may be used as a raw material in the
10 monochloropropanediol synthesis process from step a) of the process according to the invention.

 The invention also relates to an aqueous composition of which the salt content is greater than or equal to 50 g/kg of composition and of which the glycidol content is greater than or equal to 0.1 g/kg and less than or equal to
15 60 g/kg of aqueous composition, possibly being obtained according to the process described above, in which case the second fraction separated at the end of the treatment from step c) constitutes the aqueous composition.

 The aqueous composition may comprise, besides a salt and glycidol, 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol.

20 The salt content of the aqueous composition is greater than or equal to 50 g/kg, usually greater than or equal to 100 g/kg, commonly greater than or equal to 150 g/kg and in many cases greater than or equal to 200 g/kg.

 The glycidol content in the aqueous composition is greater than or equal to 0.1 g/kg, usually greater than or equal to 1 g/kg and commonly greater than or
25 equal to 2 g/kg. The glycidol content is less than or equal to 60 g/kg, usually less than or equal to 50 g/kg, commonly less than or equal to 40 g/kg and in many cases less than or equal to 35 g/kg.

 The 1,3-dichloro-2-propanol content in the aqueous composition is generally greater than or equal to 0.01 g/kg, usually greater than or equal to
30 1 g/kg and commonly greater than or equal to 2 g/kg. The 1,3-dichloro-2-propanol content is generally less than or equal to 100 g/kg, usually less than or equal to 80 g/kg and commonly less than or equal to 40 g/kg.

 The 3-chloro-1,2-propanediol content in the aqueous composition is generally less than or equal to 50 g/kg, usually less than or equal to 10 g/kg and
35 commonly less than or equal to 1 g/kg. The 3-chloro-1,2-propanediol content is generally greater than or equal to 0.1 g/kg.

The invention also relates to the use of this aqueous composition in an electrolysis process, such as defined above.

The second fraction separated at the end of the treatment from step c) may be subjected to supplementary treatments such as those described in Application
5 FR 07/55697 filed in the name of Solvay SA, of which the content, and more specifically the passages from page 3, line 30 to page 4, line 4, and from page 6, line 18 to page 20, line 31, is incorporated here by reference, and which
comprise physical treatments which may be chosen from dilution, concentration, evaporation, distillation, stripping, liquid/liquid extraction and adsorption
10 operations, alone or in combination, chemical treatments, which may be chosen from oxidation, reduction, neutralization or complexation operations, alone or in combination, and biological treatments, which may be chosen from aerobic and anaerobic bacterial treatments, alone or in combination, so as to obtain a purified saline composition.

15 This purified saline composition is an aqueous composition containing at least one salt in an amount greater than or equal to 50 g/kg of composition, of which the total organic carbon content is greater than or equal to 1 µg of C per liter and less than or equal to 1 g of C per liter of composition, which contains at least one carboxylic acid and at least one chloroether.

20 The invention also relates to the use of this aqueous composition in an electrolysis process, such as defined above.

The examples below are intended to illustrate the invention without, however, limiting it.

Example 1 (according to the invention)

25 A dehydrochlorination trial has been carried out in a vessel equipped with a jacket with a thermocouple, a magnetic bar for agitation, a pH electrode and a funnel for the addition of a caustic soda solution. Water (99.5 g) and 100.6 g of an organic mixture containing 992 g of 3-chloro-1,2-propanediol per kg, less than 0.05 g of 2-chloro-1,3-propanediol per kg, 1.4 g of 1,3-dichloro-2-propanol
30 per kg, 0.14 g of 2,3-dichloro-1-propanol per kg and 6.4 g of chloroethers per kg, have been introduced at room temperature (~25 °C) in the vessel.

A 40 % by weight NaOH aqueous solution (64.46 g, 0.64 mol) has then been introduced continuously in the vessel under agitation during 30 minutes. The temperature was constant at ~25 °C and the pH has varied in the
35 range 10.4 – 12.0. After 30 minutes, an homogeneous mixture has been obtained. The conversion rates of 1,3-dichloro-1-propanol, 2,3-dichloro-1-

propanol and 3-chloro-1,2-propanediol were respectively 96%, 6% and 69 % (98.5 % of the theoretical value). The selectivity of the formation of epichlorohydrin calculated with respect of the converted dichloropropanol was 70 % and the selectivity for the glycidol formation from 3-chloro-1,2-propanediol was 98.5 %.

Example 2 (according to the invention)

A dehydrochlorination trial has been carried out in a vessel equipped with a jacket with a thermocouple, a mechanical agitator, a pH electrode and a funnel for the addition of a caustic soda solution. Water (182.28 g) and 150.26 g of a mixture containing 662 g of 3-chloro-1,2-propanediol per kg, less than 0.05 g of 2-chloro-1,3-propanediol per kg, 300 g of 1,3-dichloro-2-propanol per kg, 34 g of 2,3-dichloro-1-propanol per kg and 4 g of chloroethers per kg have been introduced at room temperature (~ 22°C) in the vessel. A 40 % by weight NaOH aqueous solution (117.07 g, 1.17 mol) has been introduced continuously during 30 minutes. The temperature has increased from 22 °C to 32°C and the pH has varied in the range 9.5- 11.7 during the addition. The reaction mixture has been decanted and two liquid phases have been separated. The compositions of the organic fraction (22.54 g) and the aqueous fraction (422.33 g) are given in the Table 1. The conversion rates of 1,3-dichloro-1-propanol, 2,3-dichloro-1-propanol and 3-chloro-1,2-propanediol were respectively 94%, 20% and 88 %. The selectivity of the formation of epichlorohydrin calculated with respect to the converted dichloropropanol was 75.1 % and the selectivity for the glycidol formation from the converted 3-chloro-1,2-propanediol was 93.8 %.

Table 1

Constituent	Organic Fraction (g/kg)	Aqueous Fraction (g/kg)
Epichlorohydrin	663	20
Glycidol	71	126
1,3-dichloro-2-propanol	51	3.5
2,3-dichloro-1-propanol	119	3.4
3-chloro-1,2-propanediol	13	28
2-chloro-1,3-propanediol	0.3	3.1
Glycerol	< 0.05	14
Chloroethers (C6 and C9)	33	24

Example 3 (according to the invention)

A part of the mixture obtained at the issue of the reaction of example 1 (46.93 g) has been added to 54.43 g of 1,3-dichloro-2-propanol. The mixture has been vigorously stirred at room temperature during 30 min. The mixture has

then been decanted and the two liquid phases are separated. 69.89 g of a heavy organic phase and 30.08 g of a light aqueous phase have been obtained and their compositions are given in the Table 2. The major part of practically all the organic products, except glycerol, has been extracted by the solvent.

5 Table 2

Constituent	Example 1 Mixture (g/kg)	Aqueous Fraction after decantation (g/kg)	Organic Fraction after decantation (g/kg)
Epichlorohydrin	0.26	1.2	3.2
Glycidol	200	73	98
1,3-dichloro-2-propanol	< 0.05	39	Solvent
2,3-dichloro-1-propanol	0.05	0.13	1.7
3-chloro-1,2-propanediol	117	42	62
2-chloro-1,3-propanediol	n.d.	n.d.	n.d.
Glycerol	0.26	0.35	< 0.05
Chloroethers (C6 and C9)	6.5	2.5	4.3

CLAIMS

1 - Process for manufacturing glycidol comprising at least the following steps:

a) glycerol and a chlorinating agent are reacted to form monochloropropanediol in a first reaction medium; and

5 b) at least one basic compound is reacted with at least one part of the first reaction medium from step a) to form glycidol and a salt in a second reaction medium, the organic component of which has a monochloropropanediol content before reaction with the basic compound greater than 100 g/kg of organic component.

10 2 - Process according to Claim 1, in which the reaction from step a) is carried out at a temperature greater than or equal to 20°C and less than or equal to 300°C, at a pressure greater than or equal to 0.3 bar absolute and less than or equal to 100 bar absolute and over a duration greater than or equal to 0.5 h and less than or equal to 20 h when the reaction step a) is carried out in batch mode
15 or for a residence time greater than or equal to 1 h and less than or equal to 50 h when the reaction step a) is carried out in continuous mode.

3 - Process according to Claim 1 or 2, in which the second reaction medium from step b) comprises a single liquid phase.

20 4 - Process according to any one of Claims 1 to 3, comprising at least one supplementary step c) in which at least one part of the second reaction medium from step b) is subjected to at least one treatment chosen from settling and liquid/liquid extraction operations, alone or in combination, at the end of which treatment a first fraction containing most of the glycidol which was contained in the part of the second reaction medium from step b) before the treatment from
25 step c) and a second fraction containing most of the salt which was contained in the part of the second reaction medium from step b) before the treatment from step c) are separated.

5 - Organic composition of which the glycidol content is greater than or equal to 100 g/kg of organic composition and of which the 3-chloro-1-propanol
30 content is greater than or equal to 0.005 g/kg and less than or equal to 2 g/kg of

organic composition, possibly being obtained according to the process from Claim 4, in which case the first fraction separated at the end of the treatment from step c) constitutes the organic composition.

5 6 - Aqueous composition of which the salt content is greater than or equal to 50 g/kg of aqueous composition and of which the glycidol content is greater than or equal to 0.1 g/kg and less than or equal to 60 g/kg, possibly being obtained according to the process from Claim 4, in which case the second fraction separated at the end of the treatment from step c) constitutes the aqueous composition.

10 7 - Process for purifying the organic composition according to Claim 5 via at least one treatment chosen from dilution, concentration, evaporation, distillation, stripping, liquid/liquid extraction and adsorption operations, alone or in combination, so as to obtain a purified glycidol-based product.

15 8 - Purified glycidol-based product of which the glycidol content is greater than or equal to 900 g of glycidol per kg of product, and of which the halogenated hydrocarbon content is less than or equal to 1 g/kg of product.

20 9 - Process for purifying the aqueous composition according to Claim 6 via at least one treatment chosen from dilution, concentration, evaporation, distillation, stripping, liquid/liquid extraction and adsorption operations, alone or in combination, so as to obtain a purified saline aqueous composition.

25 10 - Purified saline aqueous composition containing at least one salt in an amount greater than or equal to 50 g/kg of composition, of which the total organic carbon content is greater than or equal to 1 µg of C per liter and less than or equal to 1 g of C per liter of composition, which contains at least one carboxylic acid and at least one chloroether.

30 11 - Use of the organic composition according to Claim 5 or of the purified glycidol-based product according to Claim 8 as a stabilizer in natural oils and vinyl polymers, as a reaction intermediate in the manufacture of polyglycerols, glycerol, glycidyl ethers, glyceryl ethers, esters and amines, as a reactant in processes for manufacturing functionalized epoxides such as 2,3-epoxypropyloxy chloroformate and 2,3-epoxypropyl urethanes, as an alkylating agent, as an anti-emulsifier and for stabilizing milk of magnesia.

12 - Use of the aqueous composition according to Claim 6 or of the purified saline aqueous composition according to Claim 10 in an electrolysis process.